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THE ETHYNYL RADICAL C_2H—A NEW INTERSTELLAR MOLECULE

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ABSTRACT

Four new interstellar lines have been detected in a number of galactic sources with derived rest frequencies of 87,317.05, 87,328.70, 87,402.10, and 87,407.23 MHz. Based on laboratory ESR data in the solid state, these lines have been positively identified as hyperfine components of the $N = 1 \rightarrow 0$ transition of the ethynyl radical C_2H. The astronomical observations yield precise values for the C_2H rotation, spin-doubling, and hyperfine constants, namely, $2B_0$–$4D_0$ = 87,348.74 ± 0.19 MHz, $\gamma = -62.57 \pm 0.13$ MHz, $b = 40.24 \pm 0.43$ MHz, and $c = 12.23 \pm 0.35$ MHz. Ethynyl is apparently one of the most abundant interstellar polyatomic molecules with column densities in the best sources $\sim 10^{15}$ cm^{-2}. In the Orion Nebula the north-south extent of C_2H emission is nearly a quarter of a degree.

Subject headings: molecules, interstellar — radio lines

We have detected four new interstellar lines near 87.3 GHz and have positively identified them as hyperfine components of the lowest rotational transition of the ethynyl radical, C_2H. Though never before observed in the terrestrial laboratory in the gas phase, C_2H turns out to be one of the most abundant interstellar polyatomic molecules yet detected. These observations are the first spectroscopic study of the free C_2H radical, and have yielded precise values for its microwave constants.

The lower-frequency doublet shown in figure 2 was first detected in the Orion Nebula in 1973 November during the course of other observations on the 36-foot (11 m) telescope of the National Radio Astronomy Observatory.[1] A search of nearby frequencies revealed the presence of a second doublet 80 MHz higher in frequency. By the end of a second observing session in 1974 February, the full quartet had been detected in six sources and the lower-frequency pair in seven more. Limited maps of the four lines were made in Orion and DR21. A summary of the observational data is given in table 1.

In our attempts to identify the new lines we noted that the observations provided compelling evidence that all four lines arise from a single molecule. Wherever observed, the four lines have approximately the same widths; their frequency separation and (to within the noise level) relative intensities never change with position. The rest frequencies and relative intensities derived from the data in Orion A are given in table 2.

We were quickly able to convince ourselves that these new lines could not be identified with any known interstellar molecule or even with any molecule whose microwave constants had ever been measured in the laboratory. Neither a simple rigid-rotor calculation nor direct laboratory measurement for molecules with centrifugal distortion, internal rotation, or inversion turned up a molecule which could explain more than one of the observed lines. The obvious implication was that the interstellar lines are being produced by a molecular species which is so reactive that its microwave spectrum had not yet been measured.

From the beginning the C_2H radical was considered a plausible candidate, since its lowest-frequency rotational transition is expected to be at about the right frequency, and spin doubling and hyperfine structure (hfs) should produce structure on about the scale we observe. Although the free C_2H radical has never been observed in the laboratory, nonrotating C_2H trapped in inert gas matrices at liquid helium temperatures has been studied extensively by electron spin resonance (ESR), infrared, and optical spectroscopy (Cochran, Adrian, and Bowers 1964; Graham, Dismuke, and Weltner 1974). From these investigations it is known that C_2H is linear, and like its isoelectronic counterpart CN its electronic ground state is $^2\Sigma$. The ESR measurements of the hyperfine structure are the essential foundation of our identification of C_2H.

We obtain a simple estimate of the C_2H rotation constant by assuming the bond lengths in C_2H are the same as in acetylene. This yields a frequency for the lowest rotational transition, $\nu_{10} = 2B_0 = 88.4$ GHz—only 1 GHz above our lines. To estimate how much the acetylene bond lengths might change upon removal of an H atom, we note that the removal of the H from HCN, which is isoelectronic with C_2H_2, causes the C≡N bond to expand by 0.018 Å. The effect of a similar increase in the C≡C bond in C_2H would be to lower ν_{10} by 2.1 GHz, to a frequency 1 GHz below our lines. Finally, we note that an ab initio calculation of

[1] Operated by Associated Universities, Inc., under contract with the National Science Foundation.

TABLE 1

SUMMARY OF C_2H OBSERVATIONS

SOURCE (1)	α(1950) (2)	δ(1950) (3)	v_{LSR} (km s^{-1}) (4)	Δv (km s^{-1}) (5)	T_R (° K) (3/2, 2) → (1/2, 1) (6)	(3/2, 1) → (1/2, 0) (7)	(1/2, 1) → (1/2, 1) (8)	(1/2, 0) → (1/2, 1) (9)
W3	$2^h21^m55^s$	61°52′00″	−39.6	6.9	0.52±0.08	0.23±0.08	...	...
W3(OH)	2 23 17	61 38 59	−48.0	4.6	0.71±0.07	0.31±0.07	...	...
Ori A:								
8′ S	5 32 47	−5 32 21	8.5	5.0	0.55±0.20	<0.5	...	...
6′ S	...	30 21	8.5	5.3	0.96±0.16	0.69±0.16	...	...
4′ S	...	28 21	8.5	4.3	1.80±0.21	1.00±0.21	...	...
3′ S	...	27 21	8.5	3.7	1.48±0.22	0.90±0.22	0.41±0.12	0.36±0.12
2′ S	...	26 21	8.5	4.3	1.20±0.11	0.59±0.11	0.73±0.09	0.35±0.09
1′ S	...	25 21	8.5	3.8	1.31±0.13	0.74±0.13	0.82±0.08	0.56±0.08
KL Nebula	...	24 21	8.7	3.7	1.97±0.14	0.96±0.14	0.87±0.11	0.40±0.11
1′ N	...	23 21	9.5	2.8	2.53±0.25	1.66±0.25	1.72±0.13	0.67±0.13
2′ N	...	22 21	9.7	2.2	3.83±0.12	2.11±0.12	1.95±0.12	0.95±0.12
4′ N	...	20 21	10.2	2.1	1.98±0.30	0.93±0.30	0.95±0.20	0.64±0.20
6′ N	...	18 21	...	...	<1.8	<1.8	...	...
8^s E	5 32 55	24 21	...	...	<1.0	<1.0	...	...
8^s E,2′ N	...	22 21	8.7	4.5	0.90±0.32	0.56±0.32	...	...
NGC 2024	5 39 12	−1 55 42	9.7	2.8	0.88±0.25	0.43±0.25	...	...
NGC 2264	6 30 29	9 32 12	7.5	4.3	0.70±0.10	0.39±0.10	0.31±0.10	0.34±0.10
IRC+10216	9 45 14	13 30 40	−32.8	30.0	0.31±0.03	0.17±0.03	0.19±0.04*	...
ρ Oph†	16 23 15	−24 19 00	3.2	2.8	0.45±0.20	0.57±0.20	...	...
Sgr A(NH_3 A)	17 42 28	−29 01 30	25.2	21.0	0.50±0.20	<0.3	...	...
Sgr B2	17 44 11	−28 22 30	53.2	24.0	0.63±0.06	0.37±0.06	...	...
M17 SW:								
12^s W‡	18 17 15	−16 14 54	21.9	3.5	0.88±0.19	0.53±0.19	<0.4	<0.4
3′ S	18 17 27	17 54	...	...	<0.5	<0.5	...	...
CO Peak	...	14 54	19.5	5.5	2.11±0.10	1.15±0.10	0.91±0.06	0.51±0.06
3′ N	...	11 54	...	...	<0.5	<0.5	...	...
12^s E	18 17 39	14 54	...	...	<0.5	<0.5	...	...
W51	19 21 27	14 24 29	56.7	9.7	1.13±0.07	0.58±0.07	0.63+0.07	0.27+0.07
DR 21	20 37 14	42 09 00	−2.4	3.4	1.49±0.09	1.02±0.09	0.79±0.06	0.42±0.06
1′30″ N	...	10.30	−2.3	3.0	1.18±0.12	0.88±0.12	0.75±0.12	0.44±0.12
DR 21(OH)	...	12 00	−4.1	3.6	1.28±0.15	0.94±0.15	0.85±0.11	0.40±0.11
NGC 7538	23 11 37	61 11 58	−56.8	5.8	0.88±0.10	0.39±0.10	...	...

NOTES TO TABLE 1.—Data were obtained with a filter bank of 256 channels each 250 kHz wide (0.86 km s^{-1}). At 87.3 GHz the half-power beamwidth was 76″. Calibration was done with a chopper wheel, according to the method of Davis and Vanden Bout (1973). At a given position no significant difference among the four lines in either radial velocity, v_{LSR}, or the full line width at half-intensity, Δv, was observed, so the tabulated values of these quantities in columns (4) and (5) are simply the weighted averages of the four lines. T_R in columns (6)–(9) is the peak line radiation temperature corrected for atmospheric absorption (defined in terms of the intensity of radiation I_ν as $T_R = \lambda^2 I_\nu/2k$); dots under this heading indicate that no observation was made.

* Blended with the $(\frac{1}{2}, 0)$–$(\frac{1}{2}, 1)$ line.

† Encrenaz 1974.

‡ Lada, Dickinson, and Penfield 1974.

TABLE 2

REST FREQUENCIES AND INTENSITIES OF THE $N = 1 \rightarrow 0$ TRANSITIONS OF C_2H

TRANSITION $J'F' \rightarrow JF$	FREQUENCY (MHz)	RELATIVE UNCERTAINTY (MHz)	ABSOLUTE UNCERTAINTY (MHz)	RELATIVE INTENSITY Theoretical	Observed
(3/2, 1)→(1/2, 1)	87,284.38*	...	...	4.25	...
(3/2, 2)→(1/2, 1)	87,317.05	0.04	0.18	41.67	39±3
(3/2, 1)→(1/2, 0)	87,328.70	0.07	0.19	20.75	22±2
(1/2, 1)→(1/2, 1)	87,402.10	0.07	0.19	20.75	19±3
(1/2, 0)→(1/2, 1)	87,407.23	0.15	0.23	8.33	11±2
(1/2, 1)→(1/2, 0)	87,446.42*	...	...	4.25	...

NOTES TO TABLE 2.—Rest frequencies were determined from the lines 2′ N of the KL nebula. The radial velocity, v_{LSR}, at this position was determined from our frequencies on the assumption that in the direction of the KL nebula $v_{LSR} = 8.7 \pm 0.6$ km s^{-1}—the average velocity and velocity dispersion calculated from the millimeter lines of nine other molecules. Uncertainties represent 1 σ. Relative uncertainties result from the statistical uncertainty in measuring line center frequencies with an estimated contribution of 25 kHz in the center frequency of each channel of the receiver (Mauzy, private communication).

* Not observed—calculated from the constants in table 3.

the ethynyl ground state by Barsuhn (1972) predicts a transition frequency of 88.9 GHz. Thus our identification is entirely consistent with existing estimates of the $N = 1 \rightarrow 0$ transition frequency of C_2H.

The ESR studies of C_2H in a matrix provide only an order-of-magnitude estimate of the spin doubling but yield precise measurements of the hfs. Spin doubling is produced by the interaction between the unpaired electron spin and the weak molecular magnetic field induced by rotation, hfs by the Fermi contact and magnetic dipole-dipole interactions of the electron and proton. There exist empirical grounds for believing that the matrix effects on the hyperfine interactions are small (argon and krypton matrices, for example, yield the same result) so that the ESR data can be applied with confidence to the free molecule.

Since the spin-doubling and hyperfine interactions are very much smaller than the rotational energy, they can be treated as first-order perturbations and calculated from the Hamiltonian (cf. Townes and Schawlow, p. 196)

$$H = \gamma\, \boldsymbol{S}\cdot\boldsymbol{N} + b\, \boldsymbol{I}\cdot\boldsymbol{S} + cI_zS_z \qquad (1)$$

where $\boldsymbol{N}$ is the total angular momentum exclusive of spin, and $\boldsymbol{S}$ and $\boldsymbol{I}$ are, respectively, the electronic ($S = \frac{1}{2}$) and proton ($I = \frac{1}{2}$) spins with components S_z and I_z along the (moving) molecular axis. The hyperfine constants, b and c, measured by ESR are given in table 3. The spin-doubling constant γ can only be roughly estimated from existing experimental data to be $\gamma = -2\, B_0\, \Delta g_\perp = -20$ MHz (Knight and Weltner 1970), where $\Delta g_\perp$ is the difference between the measured molecular g-factor and that of the free electron.

Figure 1 shows the energy level diagram for C_2H, corresponding to the angular momentum coupling scheme

$$\boldsymbol{N} + \boldsymbol{S} = \boldsymbol{J}, \quad \boldsymbol{J} + \boldsymbol{I} = \boldsymbol{F}. \qquad (2)$$

It turns out that for C_2H the pure coupling scheme is not too good an approximation since the hyperfine splittings are not small compared with the spin doubling interval. Thus, in calculating the energy levels of C_2H, matrix elements off-diagonal in J cannot be neglected. Electric dipole selection rules require $\Delta F = 0, \pm 1$ ($0 \not\leftrightarrow 0$), so that the $N = 1 \rightarrow 0$ transition is split into six hyperfine components.

In order to determine whether the observed lines are indeed produced by C_2H, we calculated theoretical

TABLE 3

ROTATIONAL, SPIN-DOUBLING, AND HYPERFINE CONSTANTS OF C_2H

Constant	This Work (MHz)	Electron Spin Resonance* (MHz)
$\nu_{10} = 2B_0 - 4D_0$	87,348.74±0.19	...
γ	−62.57±0.13	...
b	40.24±0.43	40±1
c	12.23±0.35	12±3

* Graham *et al.* 1974.

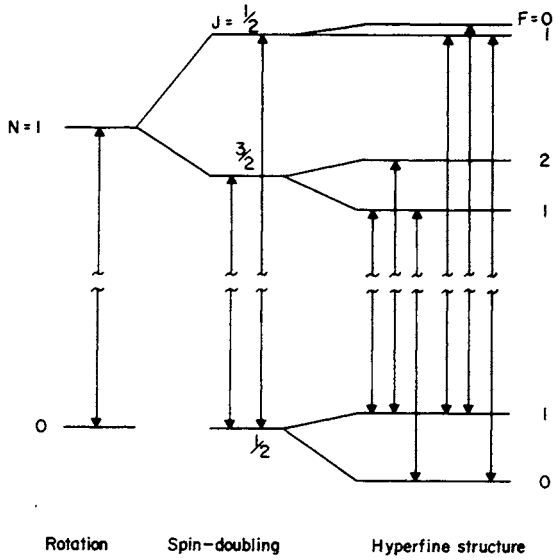

FIG. 1.—Energy level diagram of the $N = 1$ and $N = 0$ rotational levels of C_2H, showing the six allowed hyperfine transitions.

spectra using the ESR values of the hyperfine constants while allowing the unknown spin-doubling constant to vary. As figure 2 shows, we have been able to obtain a strikingly close fit between the observed lines and the four strongest hyperfine components of the $N = 1 \rightarrow 0$ transition. Essentially six independent observed quantities—three frequency intervals and three relative intensities—are fitted by one free parameter, γ, so it is evident that the possibility of a misidentification is very small. Detection of the two remaining hyperfine components, at roughly half the intensity of the weakest observed line (table 1), would provide a conclusive demonstration of our identification.

Having identified C_2H on the basis of ESR measurements, we can now relax the constraint on the hyperfine constants and calculate them along with the line center frequency, ν_{10}, and the spin-doubling constant from the observed frequencies in table 1. The slightly improved values of the hyperfine constants obtained in this way are given in table 3. The line center frequency and the spin-doubling constant, also listed in table 3, have been measured for the first time in this work.

The observations have shown that C_2H is an extremely common constituent of the interstellar medium. It has been detected in 13 of 14 sources in which it was searched for; and in Orion A a north-south strip map shows that C_2H emission extends over nearly a quarter of a degree.

In converting the measured intensities and line widths into column densities of C_2H, one must contend with the usual uncertainty in the molecular excitation and, in addition, with the fact that the C_2H dipole moment has never been measured. The observations indicate that the C_2H lines are almost certainly optically thin—the hyperfine intensities are always normal, and

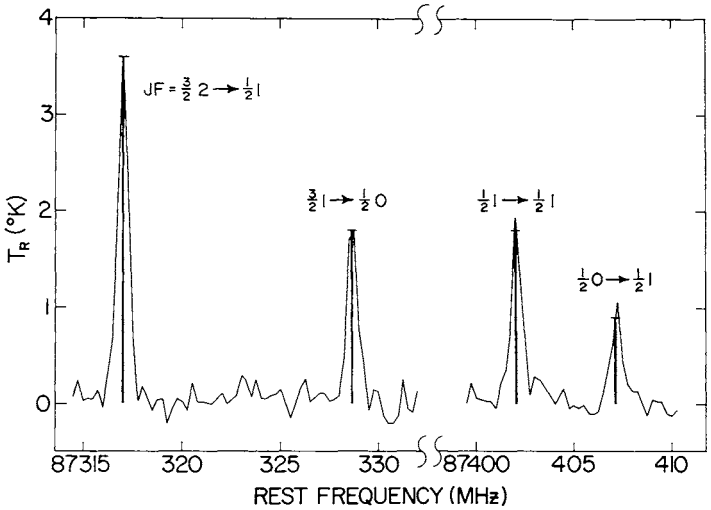

FIG. 2.—Comparison of theory and observation. The observed spectrum is that 2′ N of the KL nebula. Vertical bars represent frequencies and relative intensities of the four strongest hyperfine components of the $N = 1 \rightarrow 0$ C_2H transition, calculated using the ESR values of the hyperfine constants and the best-fit values of the spin-doubling and rotation constants.

there is no evidence of broadening due to saturation. The column density is then simply

$$N_{C_2H} = \frac{8\pi k}{hc^3 A_{10} f} \Sigma T_R \nu^2 \Delta v \,, \qquad (3)$$

where Δv and T_R are the line widths and temperatures given in table 1, f is the fractional population of the $N = 1$ level, and the summation is over the six hyperfine components. To calculate the spontaneous radiative decay coefficient A_{10} we must rely on an ab initio calculation of the C_2H dipole moment by Green (private communication 1974), who finds $\mu = 0.8 \pm 0.2$ debye, yielding $A_{10} = 1.66 \times 10^{-6}$ s^{-1}. A reasonable upper limit to the column density in the direction of the Kleinmann-Low (KL) nebula is then obtained by assuming that the energy levels of C_2H are in thermal equilibrium with the kinetic temperature, which is about 100° K (Kutner *et al.* 1973). To obtain a lower limit, we assume that only the lowest two rotational levels are populated. We then obtain, for the KL nebula,

$$5 \times 10^{14} < N_{C_2H} < 3 \times 10^{15} \text{ cm}^{-2} \,.$$

This column density is comparable to that of methanol, making C_2H one of the most abundant polyatomic molecules yet detected.

Because of its relatively small dipole moment, C_2H may be useful in studying regions of moderate density. Taking the excitation cross-section to be about that calculated for other molecules, $\sim 10^{-15}$ cm^2, one finds that densities of only $\sim 10^4$ cm^{-3} are required to produce detectable emission. Thus, in the dense molecular clouds associated with H II regions, emission from C_2H may be observable over a greater spatial extent than that from large-dipole-moment molecules, such as methanol and hydrogen cyanide, and it may even be detectable in some dark nebulae.

Our limited map in Orion shows that the C_2H lines, unlike the millimeter lines of most molecules, peak up not on the KL nebula but rather at a position 2′ north. In this respect, C_2H is similar to CN—the only other free radical observed at millimeter wavelengths. It is tempting to conclude that the fractional abundances of highly reactive species decrease as one looks at the denser parts of the cloud where they recombine to form chemically more stable molecules.

The existence of large amounts of C_2H would seem to be an important observational fact to be explained by theories of molecular formation in interstellar clouds. Ion-molecule reactions, which have been shown to produce simple molecules such as CO, CN, and HCN in approximately the right amounts (Herbst and Klemperer 1973; Watson 1974), also appear to be able to produce C_2H. Watson, in particular, notes that C_2H is a likely end product of a number of reaction chains involving the C^+ ion, and he estimates an abundance that agrees reasonably well with our results. We expect that our observations will provide impetus for further study of the effects of the existence of C_2H on the chemistry of molecular clouds.

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